

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>A61K 7/06, 7/50</b>		<b>A1</b>	(11) International Publication Number: <b>WO 95/24180</b>
			(43) International Publication Date: 14 September 1995 (14.09.95)
(21) International Application Number: PCT/EP95/00717		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).	
(22) International Filing Date: 25 February 1995 (25.02.95)			
(30) Priority Data: 9404550.7 9 March 1994 (09.03.94) GB			
(71) Applicant (for AU BB CA GB IE KE LK MN MW NZ SD SG SZ TT UG only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).		<b>Published</b> With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(71) Applicant (for all designated States except AU BB CA GB IE KE LK MN MW NZ SD SG SZ TT UG): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).			
(72) Inventor: MURRAY, Andrew, Malcolm; 15 Moorings Close, Parkgate, South Wirral, Cheshire L64 6TL (GB).			
(74) Agent: MULDER, C., W., R.; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).			
(54) Title: HAIR CONDITIONING COMPOSITION			
(57) Abstract			
<p>A rinse off hair conditioning composition comprising: (a) about 0.05 to about 5 % by weight of cationic surfactant, (b) 0.01 to 10 % by weight of an emulsion polymerised dimethiconol nonionic conditioning polymer having the formula: <math>\text{HO-Si}(\text{CH}_3)_2\text{-O-[Si}(\text{CH}_3)_2\text{-O-}]_n\text{Si}(\text{CH}_3)_2\text{-OH}</math> where n is greater than 2700, and (c) water. The invention also comprises a method of making a conditioning composition.</p>			
<p>102(b) 0.1-3, 14 19 — 0.6</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

Hair Conditioning Composition

This invention relates to hair conditioning compositions intended to be rinsed off and containing non-volatile insoluble silicone gum, particularly dimethiconol gum.

Use of high viscosity gums as hair conditioning agents is known and suitable gums are described in US 4 874 416 (Spitzer). The gums are usually used in solution in a volatile silicone such as a cyclomethicone.

Emulsion polymerised silicones are known from US 2 891 920 (Hyde), US 3 294 725 (Findlay), and US 3 360 491 (Axon).

Emulsion polymerised dimethylpolysiloxane microemulsions are described in EP 0 268 982 (Toray). Dimethiconol materials are taught as one of a range of possibilities.

Articles such as "Organofunctional Silicones for Personal Care Applications", Wendel, Samuel R and DiSapio, Alfred J. *Cosmetics & Toiletries* vol 98 May 1983, pp 103-106 have taught away from the use of Dimethiconol in hair compositions.

Dimethiconol can be prepared in various ways, one of which is emulsion polymerisation.

Silicone oils are often added to hair conditioning compositions in the form of aqueous emulsions. These emulsions are usually formed by mechanical shearing of the oil. Sometimes they are formed by chemical emulsification but this is not the same as emulsion polymerisation and does not provide the unexpected advantages of the present invention.

- 2 -

A problem with prior hair conditioning compositions has been that they either provide inadequate conditioning; or the use of high viscosity gums leads to processing difficulties. The latter problem has in the past been partially solved by the use of solvent for the gum. Such solvents are undesirable for the consumer and affect the conditioning properties of the gum.

According to the present invention a hair conditioning composition which is substantially free from anionic surfactant comprises:

(a) about 0.05 to about 5% by weight cationic surfactant,

(b) 0.01 to 10% by weight of an emulsion polymerised dimethiconol nonionic conditioning polymer having the formula:



where n is 2700 or more to give a molecular weight of over 200 000, and

(c) water.

Substantially free from anionic surfactant means that the composition contains less than 1% of anionic surfactant.

The composition preferably also comprises about 0.2 to about 20% by weight of a long chain fatty alcohol.

Preferably the average particle size of the dimethiconol polymer is less than 20 microns and more preferably it is less than 2 microns. Small particle size enables a more uniform distribution of silicone conditioning agent on the hair for the same concentration of silicone in the shampoo.

- 3 -

The polymer can be cross-linked. Advantageously the viscosity of the dimethiconol lies in the range 1-20 million. cst because higher viscosity increases the conditioning effect obtainable from the silicone.

5

The cationic surfactant is preferably present in an amount of 0.1 to 1% by weight. Mono-, di- and tri-alkyl substituted quaternary ammonium cationic surfactants may be used; also ethoxylated quaternary ammonium cationic surfactants. Suitable cationic surfactants include: Cetyl trimethyl ammonium chloride, Behenyl trimethyl ammonium chloride, Stearyl dimethylbenzyl ammonium chloride, cetylpyridinium chloride, and materials given the CTFA designations: Quaternium-5, Quaternium-31, Quaternium-18, and mixtures thereof. The preferred cationic surfactants are Cetyl trimethyl ammonium chloride and behenyl trimethyl ammonium chloride.

10

15

20

25

Long chain fatty alcohols may have fatty alkyl or alkenyl chains with 14 to 22 carbon atoms, preferably 16 to 20. Fatty alcohol which is particularly suitable for use in conjunction with cationic surfactant is a mixture of cetyl and stearyl alcohols. Preferably the composition comprises 0.5 to 10% by weight of long chain fatty alcohol, most preferably from 1 to 5% by weight.

The composition may also contain optional nonionic and amphoteric surfactant.

30

The nonionic surfactants suitable for use in the composition of the invention may include condensation products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally 6-30 EO.

35

- 4 -

Other suitable nonionics include mono or di alkyl alkanolamides or alkyl polyglucosides. Examples include coco mono or diethanolamide, coco mono isopropanolamide, and coco di glucoside.

5

The amphoteric surfactants suitable for use in the composition of the invention may include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines, alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutameates wherein the alkyl and acyl groups have from 8 to 18 carbon atoms. Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

10

15

20

The composition may also include minor amounts of other ingredients such as antibacterial agents, foam boosters, pearlescers, perfumes, dyes, colouring agents, preservatives, thickeners, proteins, polymers, phosphate esters and buffering agents.

25

30

The invention also comprises a method for preparation of a conditioning composition which contains insoluble silicone having a molecular weight above 200 000 and a viscosity of greater than 1 million cst as the conditioning agent comprising the steps of forming the silicone into an emulsion, the emulsion having a viscosity of less than 1000cps, then mixing the emulsion with the other ingredients. Preferably the emulsion comprises greater than 40% by weight of the silicone.

35

In a preferred method the silicone is emulsion polymerised because such a material is able to combine small particle size with high viscosity.

- 5 -

Dimethiconol silicone is particularly preferred. The dimethiconol silicone can either be used as such or it can be end-capped with a further methyl group.

5 The invention will now be further described with reference to the following examples:

Table 1

10

15

20

	A	B	1	2	3	4	5
CTAC <sup>1</sup>	0.7	0.7	0.7	0.7	0.5	0.7	-
BTAC <sup>2</sup>	-	-	-	-	-	-	0.7
Laurex CS <sup>3</sup>	1.9	1.9	1.9	3.5	1.0	1.9	1.9
Paraffin Wax	1.0	1.0	1.0	1.0	-	1.0	1.0
Glycerol monostearate	0.7	0.7	0.7	0.7	-	0.7	0.7
Natrosol 250 HR <sup>4</sup>	-	-	-	-	1.3	-	-
Polysurf 67 <sup>5</sup>	-	-	-	-	-	0.2	-
X2-1766 <sup>6</sup>	-	-	1.7	-	3.3	-	2.5
X2-1784 <sup>7</sup>	-	-	-	2.0	-	6.0	-
BY 22-026 <sup>8</sup>	-	2.0	-	-	-	-	-
minors		as	req	uir	ed		
water		to	100	%			

1 is Cetyl trimethyl ammonium chloride

25

2 is behenyl trimethyl ammonium chloride

3 is 2:1 hexadecanol:octadecanol ex Albright & Wilson

- 6 -

4 is hydroxy ethyl cellulose ex Hercules

5 is cetyl hydroxyethyl cellulose ex Hercules

5 6 is a 60% silicone emulsion polymer, mol wt 300,000

7 is a 50% silicone emulsion polymer, mol wt 240,000

8 is a 50% mechanical emulsion of silicone, mol wt 115,000

10

The compositions detailed in Table 1 were used to treat identical hair switches which were then subjected to a series of paired comparison tests by trained panellists.

15

The two attributes considered to be most indicative of conditioning benefit are (a) ease of dry combing and (b) smooth feel of the hair when dry. In each case the

20

comparison was with the comparative example A which contained no silicone conditioning agent. Comparative Example B, containing a mechanical emulsion of silicone conditioning agent according to the prior art, did not give rise to any statistically significant differences. Whereas all the compositions according to the invention were statistically preferred over Comparative Example A. From

25

these comparative tests it can be concluded that compositions according to the invention and prepared according to the method of the invention give superior results to the mechanical silicone emulsion composition B.

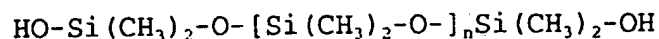


- 7 -

## CLAIMS

1. A rinse off hair conditioning composition substantially free from anionic surfactant comprising:

(a) about 0.05 to about 5% by weight of cationic surfactant,  
(b) 0.01 to 10% by weight of an emulsion polymerised dimethiconol nonionic conditioning polymer having the formula:



where n is greater than 2700, and

(c) water.

2. A composition according to claim 1 wherein the average particle size of the dimethiconol polymer is less than 20 microns.

3. A composition according to claim 2 wherein the average particle size of the dimethiconol polymer is less than 2 microns.

4. A composition according to claim 1 wherein the viscosity of the dimethiconol lies in the range 1-20 million cst.

5. A composition according to any preceding claim which further comprises 0.2 to 20% by weight of a C<sub>14-22</sub> alcohol.

6. A composition according to any preceding claim wherein the cationic surfactant is selected from the group

- 8 -

comprising cetyl trimethyl ammonium chloride and behenyl trimethyl ammonium chloride.

- 5           7.   A method for preparation of a rinse off conditioning composition which contains a cationic surfactant and insoluble silicone having a molecular weight above 200 000 and a viscosity of greater than 1 million cst as the conditioning agent comprising the steps of forming the silicone into an emulsion, the emulsion having a
- 10           viscosity of less than 1000cps, then mixing the emulsion with the other conditioner ingredients including the cationic surfactant.
- 15           8.   A method as claimed in claim 7 wherein the emulsion comprises more than 40% by weight of the silicone.
9.   A method according to claim 7 or 8 wherein the silicone is emulsion polymerised dimethiconol.

20

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 95/00717

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61K7/06 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,93 19723 (ALBERTO CULVER COMPANY) 14 October 1993 see the whole document ---	1,2,5,9
Y	EP,A,0 268 982 (TORY SILICONE COMPANY, LTD.) 1 June 1988 cited in the application see page 1, line 1 - line 35 see page 4, line 16 - line 36 see claims 1,2 ---	1,2,5,9
A	WO,A,92 09264 (RICHARDSON-VICKS, INC.) 11 June 1992 see the whole document ---	1-9
A	US,A,4 950 468 (SUNSTAR KABUSHIKI KAISHA) 21 August 1990 see the whole document ---	1-9
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

16 August 1995

Date of mailing of the international search report

25.08.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Sierra Gonzalez, M

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 95/00717

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,2 891 920 (J. F. HYDE) 23 June 1959 cited in the application see the whole document -----	1-9

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 95/00717

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9319723	14-10-93	AU-B- 3814893 CA-A- 2131029 US-A- 5332569	08-11-93 14-10-93 26-07-94
EP-A-0268982	01-06-88	JP-B- 4062288 JP-A- 63130512 AU-B- 615423 AU-A- 8327187 DE-A- 3777763 WO-A- 8803792	05-10-92 02-06-88 03-10-91 16-06-88 30-04-92 02-06-88
WO-A-9209264	11-06-92	US-A- 5073371 US-A- 5073372 AU-A- 9101091 CA-A- 2095607 CN-A- 1063038 EP-A- 0559786 FI-A- 932454 JP-T- 6503086 NZ-A- 240795	17-12-91 17-12-91 25-06-92 31-05-92 29-07-92 15-09-93 28-05-93 07-04-94 27-06-94
US-A-4950468	21-08-90	NONE	
US-A-2891920	23-06-59	NONE	